

# PATENT SPECIFICATION

NO DRAWINGS

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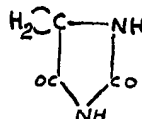
## COMPLETE SPECIFICATION

### Vinyl Hydantoins

We, BRITISH OXYGEN RESEARCH AND DEVELOPMENT LIMITED, a British Company, of Bridgewater House, Cleveland Row, St. James's, London, S.W.1, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

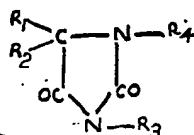
This invention relates to vinyl derivatives of substituted hydantoins, to processes for preparing, polymerising and co-polymerising them and to the polymers and copolymers so formed.

The parent compound, hydantoin, itself, which has the formula:—



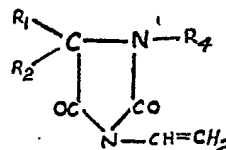
was first isolated in 1834 from the leaf buds of *plantanus orientalis*, and since that time hydantoin and many of its derivatives have been synthesised.

According to one aspect of the present invention, there are provided as new chemical compounds, vinylhydantoins of the general formula:—

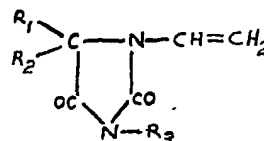


where R<sub>1</sub> is an alkyl group and R<sub>2</sub> is an alkyl, carbo-alkoxy-alkyl, aryl, aralkyl, cycloalkyl, cycloalkylalkyl, aralkenyl, or heterocyclic group; or R<sub>1</sub> and R<sub>2</sub> form a polymethylene ring or an alkyl substituted polymethylene ring; R<sub>3</sub> is a vinyl group, or an alkyl or aryl group and R<sub>4</sub> is a vinyl group, or an acyl group, or hydrogen; at least one of the groups R<sub>3</sub> and R<sub>4</sub> being a vinyl group.

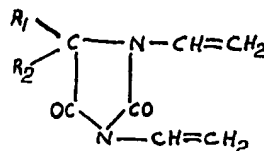
The vinylhydantoins of the present invention thus include 3-vinylhydantoins, of the general formula:—



1-vinylhydantoins, of the general formula:—

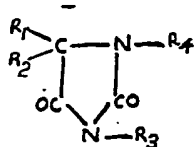


and 1:3-divinylhydantoins of the general formula:—



$R_1$ ,  $R_2$ ,  $R_3$ , and  $R_4$  in these formulae having the same significance as before.

According to another aspect of the invention, a process for the preparation of a vinylhydantoin of the formula:—



where  $R_1$  is an alkyl group and  $R_2$  is an alkyl, carbo-alkoxy-alkyl, aryl, aralkyl, cycloalkyl, cycloalkylalkyl, aralkenyl, or heterocyclic group; or  $R_1$  and  $R_2$  together form a polymethylene ring or an alkyl substituted polymethylene ring;  $R_3$  is a vinyl group, or an alkyl or aryl group; and  $R_4$  is a vinyl group, or an acyl group, or hydrogen, at least one of the groups  $R_3$  and  $R_4$  being a vinyl group, comprises reacting the substituted hydantoin corresponding to the above formula in which the vinyl group or groups are replaced by a hydrogen atom or atoms, in solution or suspension in an inert liquid with acetylene at a pressure within the range 1 to 30 atm. and at a temperature within the range 140—250° C. in the presence of a vinylation catalyst.

Suitable inert liquids for use in this process include hydrocarbons, such as benzene, toluene, xylene and kerosene, and halogenated hydrocarbons, such as chlorobenzene, but the invention is not limited to these particular classes of inert liquid.

Suitable catalysts for the reaction are cadmium salts of weak acids, in particular cadmium acetate. Zinc salts of weak acids, or mixtures of zinc salts with cadmium salts, can also be used, but in general have been found to be somewhat less efficient. Cadmium oxide, or zinc oxide, or mixtures thereof, may also be used as the catalyst.

If desired, a polymerisation inhibitor may be added to the reaction mixture; examples of suitable polymerisation inhibitors are hydroquinone, catechol and  $\beta$ -naphthylamine.

The vinylation reaction may be effected by saturating the solution or suspension of the vinylhydantoin with acetylene in a suitable vessel, for example, a stainless steel autoclave, and maintaining the solution or suspension at the required conditions of temperature and pressure until the required amount of acetylene has been absorbed. It has been observed that, in general, the reaction proceeds in a more satisfactory manner if the reaction mixture is maintained anhydrous.

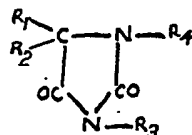
Agitation during the reaction may be provided by means of a stirrer, or by rocking or shaking the autoclave or other vessel. Alternatively, vinylation may be brought about by continuously pumping acetylene through the solution or suspension of the substituted

hydantoin held under the required conditions of temperature and pressure in a suitable vessel, the stream of acetylene gas passing through the liquid serving to agitate the mixture.

When starting with a substituted hydantoin in which both the 1- and 3-positions are vacant, a mixture of 3-mono-vinyl and 1:3-divinyl derivatives normally results from the reaction. By controlling the amount of acetylene admitted to the reaction, it is, however, possible to control the relative proportions of the two derivatives obtained, and, in particular, to obtain at least a 90% proportion by weight of the mono-vinyl derivative. It is also possible by continuing the reaction until acetylene absorption is extremely slow, to obtain a product which is predominantly the divinyl derivative. The vinylhydantoins may be separated from the crude reaction product by filtering off any suspended catalyst, followed by distillation and/or recrystallisation from a suitable solvent, which may be the inert liquid used as the reaction medium; recrystallisation may in many cases also be effected from light petroleum naphtha. The solvent and residues from the distillation stage may be returned to the reaction vessel and re-used.

The new vinylhydantoins of the present may be used to prepare polymers and copolymers.

According to a further aspect of the invention, therefore, a process for the preparation of polymers comprises polymerising a vinylhydantoin of the general formula:—

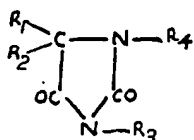


where  $R_1$  is an alkyl group and  $R_2$  is an alkyl, carbo-alkoxy-alkyl, aryl, aralkyl, cycloalkyl, cycloalkylalkyl, aralkenyl, or heterocyclic group; or  $R_1$  and  $R_2$  together form a polymethylene ring or an alkyl substituted polymethylene ring;  $R_3$  is a vinyl group or an alkyl or aryl group; and  $R_4$  is a vinyl group, or an acyl group, or hydrogen, at least one of the groups  $R_3$  and  $R_4$  being a vinyl group.

The vinylhydantoin may be polymerised in the molten state, or in solution or suspension in water or an inert organic liquid, for example, benzene. The polymerisation reaction is preferably effected at a temperature up to about 100° C. in the presence of one or more catalysts. Preferred catalysts are those generating free radicals in solution, such as, for example, benzoyl peroxide, hydrogen peroxide and azobisisobutyronitrile.

According to yet another aspect of the invention, a process for the preparation of co-

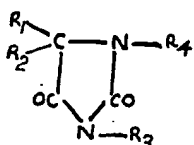
polymers comprises polymerising two or more vinylhydantoin of the general formula:—



where  $R_1$  is an alkyl group and  $R_2$  is an alkyl, carbo-alkoxy-alkyl, aryl, aralkyl, cycloalkyl, cycloalkylalkyl, aralkenyl, or heterocyclic group; or  $R_1$  and  $R_2$  together form a polymethylene ring or an alkyl substituted polymethylene ring;  $R_3$  is a vinyl group or an alkyl or aryl group; and  $R_4$  is a vinyl group or an acyl group or hydrogen, at least one of the groups  $R_3$  and  $R_4$  being a vinyl group.

The polymerisation conditions which may be used for such copolymerisation will be the same as those which may be used for the polymerisation of a single vinylhydantoin.

According to a further aspect of the invention, a process for the preparation of copolymers comprising copolymerising at least one vinylhydantoin of the general formula:—



where  $R_1$  is an alkyl group and  $R_2$  is an alkyl, carbo-alkyl-alkyl, aryl, aralkyl, cycloalkyl, cycloalkylalkyl, aralkenyl, or heterocyclic group; or  $R_1$  and  $R_2$  together form a polymethylene ring or an alkyl substituted polymethylene ring;  $R_3$  is a vinyl group or an alkyl or aryl group, and  $R_4$  is a vinyl group, or an acyl group, or hydrogen, at least one of the groups  $R_3$  and  $R_4$  being a vinyl group, with at least one compound containing at least one ethylenic linkage.

The particular polymerisation technique used in the preparation of such copolymers will depend on the nature of the comonomers present, and polymerisation procedures known in the art, including bulk, solution, suspension and emulsion polymerisation, may be used.

The nature of the polymers and copolymers produced in accordance with this invention varies considerably in accordance with the substituents in the hydantoin ring, the method of polymerisation used, and the nature and proportion of the comonomer if one is present.

The invention is illustrated by the following examples in which all parts and percentages are by weight unless otherwise indicated.

#### EXAMPLE 1.

A stainless steel rocking autoclave (working capacity 1200 cc.) was charged with 5:5-dimethylhydantoin (200 parts), cadmium acetate (10 parts), hydroquinone (2 parts) and xylene (350 parts). After closing the auto-

clave, the air was flushed out by means of nitrogen and the rocked contents were then saturated with acetylene to 5 atmospheres gauge pressure. The temperature was raised during three hours to 170° C. at which point reaction commenced as indicated by a drop in the pressure. The temperature was maintained at 170—175° C. for 12 hours and the pressure maintained at 18—20 atmospheres gauge by the introduction of further amounts of acetylene. The total fall of pressure over the 12-hour period (i.e. the summation of the several falls from 20 to 18 atm.) was 75 atmospheres. This corresponded to the introduction of about 32 parts of acetylene. (The theoretical amount of acetylene required for the production of 3-vinyl-5:5-dimethylhydantoin corresponds to 33.8 parts).

At the end of the reaction period the autoclave was cooled, the surplus acetylene was vented and the contents of the autoclave were fractionally distilled, first at atmospheric pressure to remove xylene and finally at a pressure of 0.7 mm. mercury. 3-vinyl-5:5-dimethyl-hydantoin (106 parts) distilled as a pale yellow, viscous oil at 110—115° C., followed by a higher boiling fraction (130—160° C.), which consisted mainly of unchanged starting material (18 parts).

The 3-vinyl-5:5-dimethyl-hydantoin crystallised after standing for a few minutes and it was further purified by recrystallisation from petroleum ether, from which it separated in colourless rhombs, m.p. 94° C.; analysis:—C: 55.0%; H: 6.7%; N: 17.9%; calculated for  $C_7H_{10}N_2O_2$ :—C: 54.6%; H: 6.5%; N: 18.2%. Catalytic hydrogenation in ethanol of 0.3024 gram of the new compound, using palladium on charcoal as catalyst, showed an absorption of 44 ml. hydrogen, which is exactly the calculated amount for a vinyl dimethylhydantoin. The resulting 3-ethyl-5:5-dimethylhydantoin melted at 97° C.; this differs from the melting point of 1-ethyl-5:5-dimethylhydantoin described by Blitz and Slotta in *J. für Praktische Chem.*, 1926, (2), Vol. 113, page 62, indicating that the vinyl derivative prepared is the 3-substituted compound.

#### EXAMPLE 2

4 g. 3-Vinyl-5:5-dimethylhydantoin was mixed with 0.04 g. azobisisobutyronitrile, sealed in a glass vessel in a nitrogen atmosphere and heated at 100° C. for 10 hours. The product was a very hard, transparent solid, which was ground to a powder and extracted for 12 hours with boiling toluene to remove unchanged monomer. The weight of polymer obtained was 3.8 g. It was insoluble in the common organic solvents; it was not very soluble in water although it became gel-like on the surface after long contact, or on boiling. The polymer did not melt below about 260° C. and it required a temperature of about 300° C. for moulding.

## EXAMPLE 3

Ten milligrams of azobisisobutyronitrile were added at 80° C. to a solution of 1 g. of 3-vinyl-5:5-dimethylhydantoin in 8 ml. of water. After about one minute at this temperature there was a heavy separation of a white curd-like material. The polymer when first isolated was a plastic- dough-like substance, which changed to a hard, horny solid on standing in air.

## EXAMPLE 4

To a solution of 1 g. 3-vinyl-5:5-dimethylhydantoin in 30 g. of water at 70° C. was added 0.05 g. of hydrogen peroxide (100 vols.) and one drop of concentrated aqueous ammonia solution. After one hour at 70° C., separation of polymer in the form of a colourless, tacky gel was apparent. The polymer changed to a horny solid on drying in air.

A similar product was obtained when 0.05 g. potassium persulphate was employed instead of hydrogen peroxide and ammonia.

## EXAMPLE 5

A mixture of 20 g. 3-vinyl-5:5-dimethylhydantoin, 200 ml. benzene, 0.02 ml. di-tertiarybutyl peroxide and 0.04 g. azobisisobutyronitrile was placed in a glass vessel and stirred at 70° C. in a nitrogen atmosphere for 3 hours. Polymer separation began in about ten minutes, and at the end of the period the whole consisted of a thick, gelatinous mass. The solvent was removed by distillation in vacuum. The bulky, white powder which remained was extracted with hot acetone. The polymer weighed 19 grams and was insoluble in all the common organic solvents.

## EXAMPLE 6

Fifty grams 3-vinyl-5:5-dimethylhydantoin was thoroughly mixed with 0.05 g. di-tertiarybutyl peroxide and 0.1 g. azobisisobutyronitrile in a ball mill.

Alternatively, the mixed catalysts were dissolved in a solution of the vinyl compound in diethyl ether, the volatile solvent then being removed in vacuo.

The mixture was placed in the glass lining of a stainless steel autoclave, and heated without stirring and under a pressure of 40 atmospheres of nitrogen. An exothermic reaction set in at 70° C. which caused the temperature to rise to 150° C. in 2 minutes. The colourless glass-like product which had many bubbles in it was powdered in a mortar and thoroughly extracted with hot acetone. The polymer gave a colourless disc on moulding at 325° C. and 4 tons per sq. in.

## EXAMPLE 7

Fifteen grams of 3-vinyl-5:5-dimethylhydantoin and 0.15 gram benzoyl peroxide were dissolved in sixty grams of vinyl acetate and added to 150 ml. distilled water containing 0.45 grams polyvinylalcohol. The mixture was stirred vigorously at 70–90° C. until refluxing ceased. The mixture was cooled and the beads were collected and dried in vacuo

at 60° C. The beads contained 9.8% of nitrogen which is equivalent to 54% of the vinylhydantoin in the copolymer. The latter was insoluble in hot methanol, acetone or dioxan; it softened appreciably in dimethyl-

## EXAMPLE 8

This copolymerisation was carried out in a nitrogen atmosphere at 20° C. Eight grams of 3-vinyl-5:5-dimethylhydantoin were dissolved in 32 grams of vinyl acetate and stirred with 400 g. distilled water containing 0.4 g. polyvinyl alcohol, 10 g. sodium chloride, 0.5 g. potassium persulphate, and 0.2 g. sodium metabisulphite. After stirring rapidly for 20 hours, the plastic copolymer was collected, and dried at 50° C. in a vacuum. The product was then a hard, horny solid and contained 4.7% nitrogen.

## EXAMPLE 9

Four grams of 3-vinyl-5:5-dimethylhydantoin were dissolved in sixteen grams of freshly distilled acrylonitrile and stirred into 400 g. distilled water containing 0.8 g. potassium persulphate and 0.3 g. sodium metabisulphite. After stirring at 40° C. for one hour, the copolymer was filtered off, washed, and dried at 50° C. under reduced pressure. It contained 21.3% nitrogen, corresponding to approximately 60% of acrylonitrile.

## EXAMPLE 10

A mixture of 9.0 grams vinyl toluene, 1.0 gram. 3-vinyl-5:5-dimethylhydantoin and five milligrams of benzoyl peroxide was placed in a glass tube and maintained at 80° C. for 120 hours. The product was a highly viscous fluid which solidified on cooling. After dissolution in benzene and reprecipitation by addition of methanol, the copolymer was obtained as a white asbestos-like solid containing 0.5% of nitrogen, corresponding approximately 97% vinyl toluene.

## EXAMPLE 11

Freshly distilled styrene (5 g.), 3-vinyl-5:5-dimethylhydantoin (5 g.), azobisisobutyronitrile (0.005 g.) and di-tertiarybutyl peroxide (0.005 g.) were sealed in a nitrogen atmosphere in a hard glass tube which was then heated for 16 hours at 60° C. and for 100 hours at 100° C. The cold product was powdered and extracted for several hours with hot benzene. The weight of insoluble copolymer obtained was 6.8 g.

## EXAMPLE 12

5-methyl-5-ethylhydantoin (110 parts), cadmium acetate (5.5 parts), hydroquinone (2 parts) and xylene (200 parts) were charged to the autoclave of Example 1. After purging with nitrogen the autoclave was pressurised with acetylene to 5 atmospheres gauge. The temperature was raised during three hours to 170° C. and maintained at 170–175° C. for 12 hours, the pressure being maintained at 18–20 atmospheres gauge by the introduction of further acetylene. The total fall of pressure over the 12-hour period was 21 atmo-

spheres. This corresponded to the introduction of about 18 parts of acetylene. (The theoretical amount of acetylene required for the production of 3-vinyl-5-methyl-5-ethylhydantoin corresponds to 17 parts). On working up as in Example 1, a 61% yield (80 parts) of the new vinyl compound 3-vinyl-5-methyl-5-ethylhydantoin was obtained as a yellow, viscous liquid, b.p. 106—108° C./0.4 mm., which crystallised in long stout laths, m.p. 33° C. after standing for a week. Found:—

N: 16.4%; calculated for  $C_8H_{12}N_2O_2$ :—  
N: 16.6%.

#### EXAMPLE 13

Five grams of 3-vinyl-5-ethyl-5-methylhydantoin were mixed with 0.05 g. of azobisisobutyronitrile, sealed under nitrogen in a glass tube and heated at 120° C. for 3 hours. The cooled product was powdered and extracted with boiling xylene and with boiling methanol. The cream coloured polymer (4 g.) was sparingly soluble in the common organic solvents, and its softening point was above 200° C.

#### EXAMPLE 14

The 3-vinyl derivative of 5-methyl-5-isobutylhydantoin was prepared by reacting the parent hydantoin (278 grams.) with about 80% of the calculated quantity of acetylene at 170—175°/20 atm. in the presence of cadmium acetate (13 g.) and xylene (500 g.). The unchanged 5-methyl-5-isobutylhydantoin separated out of solution on cooling the reaction product. The vinyl compound was isolated from the filtrate by distillation in vacuo (b.p. 125—130°/0.7 mm.) followed by crystallisation from light petroleum. It forms colourless crystals melting at 61—62° C. (Found: C 61.2, H 8.1, N 14.1%, the calculated values for  $C_{10}H_{16}N_2O_2$  being C 61.2, H 8.2; N 14.3%). The new vinyl compound absorbed the theoretical amount of hydrogen on shaking in the presence of a platinum catalyst to yield 3-ethyl-5-methyl-5-isobutylhydantoin, which melted at 43—44° C. (Found: C 60.9, H 9.1, N 13.5%.  $C_{10}H_{18}N_2O_2$  required C 60.5, H 9.1, N 14.1%).

#### EXAMPLE 15

A solution of 3-vinyl-5-methyl-5-isobutylhydantoin (25 g.), azobisisobutyronitrile (0.05 g.) and di-tertiarybutyl peroxide (0.05 g.) in benzene (500 ml.) was stirred in a nitrogen atmosphere at 70° C. for 40 hours. The solvent was removed at reduced pressure, the residue was then dissolved in methanol and diluted with water. The precipitate obtained was collected, washed and dried. A 1% solution of the polymer had a relative viscosity of 1.3 at 25° C., and it could be moulded into discs at about 300° C.

#### EXAMPLE 16

Into a stainless steel rocking autoclave were charged 150 parts of 5-methyl-5-phenylhydantoin, 7.5 parts of cadmium acetate, 3

parts hydroquinone and 325 parts of technical xylene. The apparatus was pressure tested by nitrogen, which was then vented, and flushed out with acetylene. The vessel was then rocked and heated to 160° C., at which point additional acetylene was pressed in to 23 atmospheres gauge. Absorption of acetylene occurred slowly at this temperature but was hastened by carrying out the reaction at 180—185° C. and 20—23 atm. pressure. The total (summed) pressure drop was restricted to 26 ats. in order to avoid the formation of the 1:3-divinyl derivative.

The product was filtered and the residue (15 parts) was washed with xylene (100 parts). The filtrate and washings were combined and distilled at reduced pressure. The principal fraction boiled at 155—158° C. at 0.3 mm. Hg. and consisted of 125 parts of a pale yellow viscous liquid which was converted into a white solid on trituration with light petroleum. The solid was recrystallised from a mixed solvent containing light petroleum and benzene in the ratio 8:1. Colourless crystals, melting point 101—102° C., of 3-vinyl-5-methyl-5-phenylhydantoin were obtained, which gave on analysis C=66.8%, H=5.5%, N=13.0%, the calculated values for  $C_{12}H_{12}N_2O_2$  being C=66.7%, H=5.6%, N=13.0%.

The compound was further characterised by catalytic hydrogenation to 3-ethyl-5-methyl-5-phenylhydantoin, colourless needles, m.p. 104° C. from light petroleum (boiling range 100—120° C.). (Found: C=66.6%, H=6.6%, N=12.9%, the values calculated for  $C_{12}H_{14}N_2O_2$  being H=6.5%, N=12.8%.

#### EXAMPLE 17

5-Undecyl-5-phenylhydantoin was prepared by heating laurophenone (235 parts) with potassium cyanide (100 parts), ammonium carbonate (200 parts) and 50% aqueous ethanol (400 parts) for 8 hours at 70—80° C. under a carbon dioxide pressure of 40 atm. It formed colourless crystals, m.p. 123° C., from ethanol. Analysis gave C=72.7%, H=9.0%, N=8.3%;  $C_{20}H_{30}N_2O_2$  requires C=72.7%, H=9.15%, N=8.5%.

A mixture of 100 parts 5-undecyl-5-phenylhydantoin, 5 parts cadmium acetate and 350 parts xylene was placed in the autoclave used in Example 1. After pressure testing with nitrogen, the vessel was charged with acetylene to 5 atm. and heated during 3 hours to 165° C. at which point further acetylene was pressed in to bring the pressure to 20 atm. The temperature was raised to the reaction temperature, 185—195° C., and the pressure maintained in the range 20—23 atm. by frequent repressurising until the required amount of acetylene had been absorbed. The crude product from the autoclave was filtered and fractionated at reduced pressure. The 3-vinyl derivative, which boiled at 240° C./0.5 mm., was a viscous liquid of refractive index

1.5242 at 20° C. and amounted to 81 parts. Analysis gave the following result: C=74.4%, H=8.8%, N=7.8%, the theoretical values for  $C_{22}H_{32}N_2O_2$  being C=74.1%, H=9.0%, N=7.9%. Hydrogenation in cyclohexane with a palladium on charcoal catalyst yielded 3-ethyl-5-undecyl-5-phenylhydantoin, refractive index  $n_D^{20} = 1.5079$ .

#### EXAMPLE 18

3-Vinyl-5-phenyl-5-undecylhydantoin (5 g.) was heated in a nitrogen atmosphere in a sealed tube with azobisisobutyronitrile (0.01 g.) and di-tertiarybutyl peroxide (0.01 g.). After 30 hours at 120°, the product was dissolved in benzene and the polymer (2.5 g.) was precipitated by addition of methanol. The polymer was a white powder with a smooth touch and it melted at approximately 180—190°.

#### EXAMPLE 19

5-Methyl-5-benzylhydantoin (106 g.) anhydrous cadmium acetate (5 g.) and hydroquinone (0.5 g.) were ground together and transferred to a stainless steel autoclave together with monochlorobenzene (500 g.). After sealing the vessel and pressure-testing with nitrogen, acetylene was pressed in to bring the pressure to 5 atmospheres gauge. The contents were agitated by a rocking motion and the temperature was raised gradually to 170° C., at which point further acetylene was introduced to raise the pressure to 23 atmospheres. The temperature was taken to 185° at which point reaction occurred as shown by a fall in the pressure. The temperature was maintained at 185—200° and the pressure at 20—23 atm. until no further acetylene was absorbed (9 hours). The dark product was filtered, the chlorobenzene was removed on the steam bath at 12 mm. pressure, and the residual viscous oil was distilled through a Claisen-type head at 20 mm. pressure. A mobile fore-run distilled over at 109—112° and the viscous main fraction was collected at 150—170°. On redistillation through a Vigreux-type column the latter boiled at 127—131°/0.9 mm. This viscous yellow oil,  $n_D^{20} 1.5540$ , was 1:3-divinyl-5-methyl-5-benzylhydantoin. Analysis gave C 70.2, H 6.2, N 11.0%, the calculated values for  $C_{17}H_{16}N_2O_2$  being C 70.3, H 6.3, N 10.9%.

#### EXAMPLE 20

A mixture of 74 g. 5-methyl-5-cyclohexylhydantoin (melting point 213° C.), anhydrous cadmium acetate (4 g.), quinol (0.5 g.) and monochlorobenzene (500 g.) was placed in a stainless steel autoclave. The free space was filled with acetylene at 5 atmospheres gauge and the vessel was rocked and heated to 170°. At this stage further acetylene was pressed in to bring the pressure to 20 atm. The temperature was raised gradually until absorption of acetylene commenced. This occurred at 215° C. and this temperature was maintained for 2 hours until the required amount of acetylene

had been absorbed.

The product was filtered, the diluent removed and the residue fractionated at 1.3 mm. pressure. The first fraction, boiling at 127—129° C. was 1:3-divinyl-5-methyl-5-cyclohexylhydantoin. This was in the form of a golden oil, refractive index 1.5275 at 20° (Found: C 67.9, H 8.2, N 11.0, the theoretical values being C 67.7, H 8.1, N 11.3%).

The main fraction, boiling range 160—165° at 1.3 mm. was also a golden oil which crystallised on trituration with methanol. After recrystallisation from light petroleum, colourless prisms melting at 120° were obtained. Analysis gave C 65.2, H 8.2, N 12.6%, the calculated value for 3-vinyl-5-methyl-5-cyclohexylhydantoin being C 64.8, H 8.2, N 12.6%.

#### EXAMPLE 21

5-methyl-5-thienylhydantoin was vinylated in the manner described in example 20. The required amount of acetylene was absorbed in 9 hours at 205° C. and 23 atm.

On cooling, the diluent was removed and the residue distilled at 2.5 mm. Only one fraction was obtained boiling at 158—161° C. This was in the form of a yellow oil which solidified on standing. The solid was recrystallised from ethanol, yielding white crystals of melting point 87—88° C. Analysis gave C 58.3, H 5.0, N 11.0, the calculated values for 1:3-divinyl-5-methyl-5-thienylhydantoin being C 58.0, H 5.0, N 11.3.

#### EXAMPLE 22

2 g of 1:3-divinyl-5-methyl-5-thienylhydantoin was warmed in a test tube with 2 mg. of azobisisobutyronitrile. After warming to 70° C. polymerisation occurred rapidly, the temperature rising to 113° C. On cooling, the product was an almost clear gel.

#### EXAMPLE 23

Ninety-two parts of 5:5-cyclohexylspirohydantoin, 5 parts of cadmium acetate, 2 parts of hydroquinone and 260 parts of technical xylene were charged into a stainless steel autoclave. The vessel was then charged with acetylene at 5 atm. The vessel and its contents were rocked and heated during three hours to 160° C., at which point more acetylene was pressed in to bring the pressure to 23 atm. No reaction was evident under these conditions and the temperature was taken to 180° C. at which point a drop in pressure occurred. The temperature was maintained at 180—200° C. and the pressure at 20—23 atm. until a total pressure of 29 atms. had taken place in 14 hours.

The cold product from the autoclave consisted of a brown powder (40 parts) and an orange-brown solution. The solid was the required 3-vinyl-5:5-cyclohexylspirohydantoin ( $C_{16}H_{14}N_2O_2$ ), which was obtained pure by crystallation from ethanol. It formed colourless needles which melted at 180° C. (Found: C 61.8; H 7.2; N 14.2%, the theoretical values for  $C_{16}H_{14}N_2O_2$  being C 61.8; H 7.3;

N 14.4%). The vinyl derivative was further characterised by reducing the vinyl group to an ethyl group by hydrogenation in ethyl acetate in the presence of a palladium catalyst. 0.995 grams of the vinyl compound absorbed 119 ml. hydrogen and yielded the hydride (3-ethyl-5:5-cyclohexylspirohydantoin), which formed glistening plates (melting at 170° C.) from ethyl acetate. Found: C 61.2; H 8.1; N 14.4%.  $C_{10}H_{16}N_2O_2$  requires C 61.2; H 8.2; N 14.3%.

A further quantity of the vinyl compound was obtained from the brown xylene solution from the autoclave by distillation at 0.4 mm. The fraction boiling at 140—160° C. partially solidified in the receiver and gave 3-vinyl-5:5-cyclohexylspirohydantoin on triturating with light petroleum.

#### EXAMPLE 24

2 g. of 3-vinyl-5:5-cyclohexylspirohydantoin was melted (at 175° C.) in a test-tube and 2 mg. of azobisisobutyronitrile was added. Polymerisation occurred immediately as indicated by a rapid rise in temperature up to 230° C. On cooling, the product was obtained as a clear yellow coloured material with a softening point of greater than 200° C.

#### EXAMPLE 25

5:5-Cyclopentylspirohydantoin (100 g.) was vinylated at 200—205° C. and 25 atmospheres pressure in a chlorobenzene medium (200 g.) in the presence of cadmium acetate (5 g.). The solvent was removed by distillation at 10 mm. pressure and the remaining mixture was distilled at 0.2 mm. The vinyl compound was obtained at 135—145° C. as a viscous pale yellow oil which solidified on cooling. On recrystallisation from light petroleum, 3-vinyl-5:5-cyclopentylspirohydantoin formed colourless crystals which melt at 107—108° (Found: C 59.9, H 7.0, N 15.5%, the values required for  $C_9H_{12}N_2O_2$  being C 60.0, H 6.7, N 15.5%). The corresponding 3-ethyl-5:5-cyclopentylspirohydantoin was readily obtained on hydrogenation in ethyl acetate with a platinum catalyst. The ethyl compound forms colourless needles melting at 113° (Found: C 59.5, H 8.0, N 15.3%;  $C_9H_{14}N_2O_2$  requires C 59.3, H 7.7, N 15.4%).

#### EXAMPLE 26

2 g. 3-vinyl-5:5-cyclopentylspirohydantoin was melted (at 108° C.) in a test tube and a few milligrams of azobisisobutyronitrile was added. An immediate rise in temperature occurred indicating polymerisation. On cooling, the product was a clear, almost colourless material with a softening point of about 200° C.

#### EXAMPLE 27

Commercial methylcyclohexanone (mainly the 2-methyl isomer) was converted into the corresponding spirohydantoin by the well known Bergs-Bucherer process.

A mixture of the hydantoin (283 g., melting range 189—193°), anhydrous cadmium

acetate (15 g.) and chlorobenzene (550 g.) was rocked in a stainless steel autoclave at 180—195° in the presence of acetylene at 20 to 23 atmosphere pressure. The calculated amount of acetylene was absorbed in 6 hours.

The cooled product was filtered, and the chlorobenzene was removed from the filtrate by distillation. The residue was then distilled at 0.9 mm., the required vinyl derivative being present in the orange, viscous fraction obtained at 175—185° C. On trituration with light petroleum, a white amorphous powder was obtained which yielded colourless needles melting at 193 after crystallising successively from ethanol and from light petroleum. Analysis gave C 63.2, H 7.8, N 13.1%, the calculated value for 3-vinyl-5:5-(2-methylcyclohexyl)-spirohydantoin,  $C_{11}H_{16}N_2O_2$ , being C 63.2, H 7.7, N 13.4%.

#### EXAMPLE 28

A mixture of 3-ethyl-5:5-dimethylhydantoin (prepared by ethylating 5:5-dimethylhydantoin as its potassium derivative with ethyl bromide in a closed vessel in known manner) (100 parts), cadmium acetate (5 parts) and xylene (250 parts) was placed in a stainless steel rocking autoclave. The assembly was then tested for pressure tightness by introducing nitrogen at 30 atm. The nitrogen was afterwards vented off and replaced by acetylene at 5 atm. The vessel was rocked and heat applied. When the temperature reached 180° C. further acetylene was pressed in to bring the pressure up to 20 atm. Reaction was apparent when the temperature had been raised to 200° C. and the temperature was maintained at 200—210° C. until there was no further absorption.

The mixture was allowed to cool to about 50° C. and the surplus acetylene was vented. The product was filtered and the xylene removed at 150 mm. pressure. The residue (106 parts) solidified on cooling and it was then dissolved in ether and shaken with 10% caustic soda solution (any unchanged material can be recovered from the alkaline extract). The ether solution was washed with water and dried with anhydrous sodium sulphate. The ether was evaporated off and the residue was crystallised from petroleum ether (boiling range 40—60° C.).

1-vinyl-3-ethyl-5:5-dimethylhydantoin formed colourless laths melting at 65—66° C. Analysis gave C=59.5, H=7.6, N=15.3%, the theoretical values for  $C_9H_{14}N_2O_2$  being C=59.3, H=7.7, N=15.4%. The substance absorbed the calculated amount of hydrogen on shaking with hydrogen in ethyl acetate in the presence of a platinum catalyst to yield 1:3-diethyl-5:5-dimethylhydantoin of refractive index 1.4644 at 20° C.

In another experiment the crude product of vinylation was fractionally distilled, whereby 1-vinyl-3-ethyl-5:5-dimethylhydantoin was obtained at 90°/1.5 mm. as a colourless oil

which rapidly crystallised on cooling.

#### EXAMPLE 29

A stainless steel rocking autoclave was charged with 300 parts of 5:5-dimethylhydantoin, 30 parts of cadmium acetate and 500 parts of xylene. The vessel was tested for leaks by the application of a pressure of 30 atmospheres of nitrogen. The nitrogen was then vented and flushed out with acetylene. A pressure of 5 atmospheres of acetylene was applied and heating and rocking of the autoclave was commenced. Absorption of acetylene was apparent at 165° C. at which point further acetylene was pressed in to bring the pressure to 23 atmospheres. The pressure was maintained at 20–23 atmospheres by periodical re-pressurising and the temperature was brought to 175–180° C. and held thereat until the absorption of acetylene had practically ceased. The product consisted of a dark-brown solid suspended in a brownish liquid. The latter was freed from xylene and distilled at a pressure of 1.5 mm. The required divinyl derivative (1:3-divinyl-5:5-dimethylhydantoin) was collected at 98–100° C. It formed a pale yellow oil, which solidified on cooling and gave long, colourless needles melting at 62–63° C. from light petroleum. Analysis gave C 60.0; H 6.6; N 15.8%, the values required for  $C_9H_{12}O_2N_2$  being C 60.0; H 6.7; N 15.6%.

The new compound on hydrogenation in ethyl acetate with a platinum catalyst absorbed the calculated volume of hydrogen and yielded 1:3-diethyl-5:5-dimethylhydantoin as colourless, hexagonal plates, melting point 65–66° C. from light petroleum. Analysis of the hydride gave C 58.6; H 8.7; N 15.2%, the values required for  $C_{11}H_{16}O_2N_2$  being C 58.7; H 8.8; N 15.2%.

#### EXAMPLE 30

A stainless steel pressure vessel of one litre capacity was charged with 100 parts 5-methyl-5-phenylhydantoin, 5 parts cadmium acetate, 2 parts hydroquinone and 250 parts of technical xylene. Heating and rocking of the autoclave was commenced at an acetylene pressure of 5 atm. At 165° C. the acetylene pressure was raised to 20 atmospheres and shortly afterwards (at 170–173° C.) absorption of acetylene was apparent by a fall in pressure. The pressure was maintained at 20–23 atmospheres by pressing in more acetylene periodically. The rate of absorption at 170–175° C. fell markedly after eleven hours. The temperature was therefore raised to 200° C. and reaction continued for a further four hours until there was no further pressure drop. The autoclave was allowed to cool to room temperature and the surplus acetylene was vented. The crude product consisted of a mobile, dark brown liquid, which was fractionated at reduced pressure. A yellow, viscous liquid was obtained at 155–159° C./2–3 mm. This substance solidified on cooling and crystallised

from ethanol in colourless needles which melted at 88° C. Analysis showed this to be the divinyl derivative of 5-methyl-5-phenylhydantoin (Found: C 69.4; H 5.8; N 11.6%). The divinyl compound  $C_{11}H_{14}N_2O_2$  requires C 69.4; H 5.8; N 11.6%. The compound was further characterised by catalytic hydrogenation: 1 gram of the material absorbed 191 ml. hydrogen and gave a colourless, viscous liquid hydride which was distilled in vacuum for analysis. Found: C 68.3; H 7.4; N 11.4%.  $C_{14}H_{18}N_2O_2$  requires C 68.3; H 7.4; N 11.4%.

#### EXAMPLE 31

1:3-Divinyl-5-methyl-5-phenylhydantoin (5 g.) was mixed with 0.05 g. azobisisobutyronitrile in benzene (15 ml.) in a glass tube. Nitrogen was passed into the mixture and the tube was then sealed and heated at 100° for 14 hours. The product was a clear, colourless gel, which was transformed into a hard white solid when the solvent was removed.

#### EXAMPLE 32

A stainless steel rocking autoclave of 1200 ml. capacity was charged with 300 g. 5-methyl-5-ethylhydantoin, 22 g. cadmium acetate, 1 g. hydroquinone and 350 g. xylene. This mixture was treated with acetylene at 20 atm. at 180–185° until the required amount had entered into reaction. The xylene was distilled from the brown, mobile liquid product, and the higher boiling material left behind was distilled at the reduced pressure of 0.6 mm. 1:3-Divinyl-5-methyl-5-ethylhydantoin boils at 74°/0.6 mm. and has refractive index at 20° C. of 1.5100 (Found: C 62.0, H 7.5, N 14.6%.  $C_{10}H_{14}N_2O_2$  requires C 61.8, H 7.3, N 14.4%). The new compound was further characterised by catalytic hydrogenation in ethyl acetate with a platinum catalyst. The theoretical amount of hydrogen was absorbed. The 1:3:5-triethyl-5-methylhydantoin is a colourless oil,  $n_D^{20}$  1.4645 (Found C 60.6, H 8.9, N 13.8%.  $C_{16}H_{22}N_2O_2$  requires C 60.5, H 9.1, N 14.1%).

#### EXAMPLE 33

In a similar manner to that described in Example 32, 200 g. of 5-methyl-5-isobutylhydantoin was reacted with acetylene at 180–190° C. The 1:3-divinyl-5-methyl-5-isobutylhydantoin (115 g.) was isolated by fractionation at reduced pressure. It is a colourless liquid, boiling at 63° C. at 0.1 mm., and refractive index 1.5004 at 20° C. (Found: C 65.0, H 8.2, N 12.7%.  $C_{12}H_{18}N_2O_2$  requires C 64.8, H 8.2, N 12.6%). On hydrogenation, it readily yielded 1:3-diethyl-5-methyl-5-isobutylhydantoin, a colourless oil,  $n_D^{20}$  1.4666 (Found: C 62.7, H 9.3, N 12.3%.  $C_{12}H_{22}N_2O_2$  requires C 62.7, H 9.8, N 12.4%).

#### EXAMPLE 34

A mixture of 5:5-cyclohexylspirohydantoin (250 g.), xylene (450 g.), cadmium acetate (25



g.) and hydroquinone (3 g.) was reacted with acetylene at 200—210° C. and 20 atm. pressure until absorption almost ceased. In this instance, it was not convenient to isolate the divinyl derivative by direct distillation owing to serious foaming of the crude product. The latter was therefore shaken with ether, filtered, the ether solution was extracted with dilute sodium hydroxide, washed with water, dried and distilled. The required 1:3-divinyl-5:5-cyclohexylspirohydantoin distilled satisfactorily at 96—98°/0.5 mm. as a colourless oil with refractive index 1.5400 at 20° C. (Found: C 65.8, H 7.3, N 12.4%.  $C_{12}H_{16}N_2O_2$  required C 65.4, H 7.3, N 12.7%). On hydrogenation the compound absorbed the calculated amount of hydrogen to yield 1:3-diethyl - 5:5 - cyclohexylspirohydantoin, a colourless oil,  $n_D^{20}$  1.4980 (Found: S 64.6, H 8.5, N 12.4%.  $C_{12}H_{20}N_2O_2$  requires C 64.3, H 9.0, N 12.5%).

#### EXAMPLE 35

5-Methyl - 5-carbethoxymethylhydantoin (melting point 137°) was prepared from acetoacetic ester by heating with a cyanide and ammonium carbonate. This hydantoin (130 g.) was placed in a stainless steel autoclave with anhydrous cadmium acetate (7 g.) hydroquinone (1 g.) and chlorobenzene (550 g.) and the mixture was rocked and heated with acetylene under pressure. The temperature was gradually raised until reaction started (at 195—200°) as judged by a drop in the pressure in the reaction vessel. Further acetylene was pressed in at this temperature to maintain the pressure in the 20—25 atm. range, until the calculated amount had been absorbed. This took 7 hours.

The product was filtered when cold, the chlorobenzene was stripped off, and the residue distilled at 1.3 mm. The majority of the product distilled at 160° C. as a very viscous orange oil. Redistillation through a Vigreux type column yielded 3-vinyl-5-methyl-5-carbethoxy-methylhydantoin as a golden yellow viscous fraction, b.p. 140—145°/0.5 mm., refractive index 1.4950 at 25°. Analysis gave the following result C 53.0, H 6.1, N 12.4%, the calculated values for  $C_{10}H_{14}N_2O_4$  being C 53.1, H 6.2, N 12.4%.

The new monomer polymerised with vigour when heated with azobisisobutyronitrile.

#### EXAMPLE 36

Cyclohexylacetone was reacted with potassium cyanide and ammonium carbonate in aqueous ethanol in the usual Bucherer method. The resulting 5-methyl-5-hexahydrobenzylhydantoin crystallised from ethanol in colourless prisms melting at 212°.

33 grams of the hydantoin were heated in a pressure vessel with cadmium acetate (2 g.), hydroquinone (0.2 g.), chlorobenzene (500 g.) and acetylene. Vinylation occurred on one hour at 195—200° C., during which time the acetylene pressure fell from 25 atm. to 21

atm. The 3-vinyl compound was isolated in the usual way, by filtration, removal of diluent, and distillation. It distilled as an orange oil at 173°/1.0 mm. On trituration with petroleum ether colourless crystals of m.p. 180° C. were obtained.

#### EXAMPLE 37

5-methyl-5-styrylhydantoin (140 g.) was mixed with cadmium acetate (7 g.), hydroquinone (1 g.) and monochlorobenzene (500 g.) in a stainless steel autoclave. After pressure testing with nitrogen, the vessel was flushed with acetylene and then acetylene was pressed in the 5 atmospheres. The vessel was then rocked and heated to 170° at which point the acetylene pressure was increased to 20 atm. Reaction occurred at 175—180° as shown by a fall in pressure. The temperature was maintained at this value, and further acetylene was pressed in from time to time to maintain the pressure in the 20—23 atm. range until the required amount had been absorbed. This took 5 hours.

The product was filtered and chlorobenzene removed at 12 mm. pressure, with water bath heating. The residue was distilled at 0.5 mm. and the vinyl derivative (75 g.) was collected at 200—210°. On triturating the orange viscous oil with light petroleum a colourless solid was obtained, which yielded colourless plates, melting at 110—111°, on crystallising from light petroleum (boiling range 60—80°). An analysis showed that the product was the required 3-vinyl-5-methyl-5-styryl-hydantoin (Found: C 70, H 5.62, N 11.4%, the theoretical values being C 69.4, H 5.8, N 11.6%).

#### EXAMPLE 38

Ten grams of the monomer prepared in the preceding example was mixed with 0.05 g. of azobisisobutyronitrile and sealed under nitrogen in a hard glass tube which was then placed in an oven at 110—120° for 36 hours. The pale brown transparent resin was dissolved in hot dimethylformamide and the solution poured into water with stirring. The white granular precipitate was filtered off and dried (weight 9.8 g.).

#### EXAMPLE 39

5:5-Dimethylhydantoin was acetylated with acetic anhydride at the boil as described in the literature (Ware, Chemical Reviews, June 1950, page 413) to obtain the 1-acetyl derivative (mp. 194°).

The acetyl compound (700 g.) was mixed with anhydrous cadmium acetate (40 g.), quinol (4 g.) and monochlorobenzene (1600 g.) in the stainless steel liner of an autoclave. Vinylation was carried out at 175—180° C. with acetylene in the pressure range 20—25 atm. until there was no further absorption (10 hours).

The cooled product was a dark brown liquid containing a small amount of solid. After filtration and removal of the diluent at water pump pressure, the dark viscous residue was

distilled at 0.4 mm. pressure. The vinyl derivative (450 g.) distilled at 82° C. as a pale greenish-yellow liquid which quickly solidified (m.p. 44° C.). Found: C 55.4, H 6.4, N 14.2%, the calculated value for 3-vinyl-1-acetyl-5:5-dimethylhydantoin,  $C_{11}H_{12}N_2O_3$ , being C 55.1, H 6.2, N 14.3%.

## EXAMPLE 40

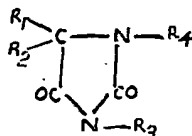
- Preparation of a terpolymer of (A) 5:5-cyclohexyl-spiro-3-vinylhydantoin, (B) 5:5-dimethyl-3-vinyl-hydantoin and (C) 5-methyl-5-ethyl-3-vinyl-hydantoin by adiabatic bulk polymerisation.

Two parts of monomer (A), one part of monomer (B) and one part of monomer (C) were melted in an autoclave with glass liner containing 0.032% of ditertiarybutylperoxide. When the melt reached approximately 100°—112° C., 0.016% of azobisisobutyronitrile was added. The autoclave was sealed and purged with nitrogen at 40 atm. The resulting adiabatically released heat of polymerisation brought the mean temperature of the block up to 150° C. A hard clear amber product was obtained, which showed high water resistance. The terpolymer was found to be thermally stable up to 275° C.

We are aware of the Home Office regulations regarding acetylene, e.g. the Compressed Acetylene Order 1947, and we make no claim to the use of this process in contravention of these regulations.

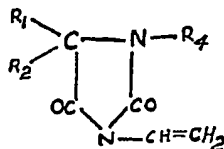
## WHAT WE CLAIM IS:—

1. Vinylhydantoin, of the general formula:—



where  $R_1$  is an alkyl group and  $R_2$  is an alkyl, carbo-alkoxy-alkyl, aryl, aralkyl, cycloalkyl, cycloalkylalkyl, aralkenyl, or heterocyclic group; or  $R_1$  and  $R_2$  together form a polymethylene ring or an alkyl substituted polymethylene ring;  $R_3$  is a vinyl group, or an alkyl or aryl group; and  $R_4$  is a vinyl group, or an acyl group, or hydrogen, at least one of the groups  $R_3$  and  $R_4$  being a vinyl group.

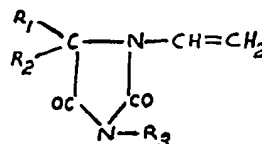
2. 3-Vinylhydantoin, of the general formula:—



where  $R_1$  is an alkyl group and  $R_2$  is an alkyl, carbo-alkoxy-alkyl, aryl, aralkyl, cycloalkyl, cycloalkylalkyl, aralkenyl, or heterocyclic group; or  $R_1$  and  $R_2$  together form a polymethylene or alkyl substituted polymethylene

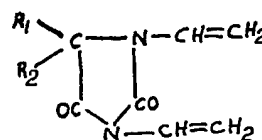
ring; and  $R_4$  is an acyl group or hydrogen.

3. 1-Vinylhydantoin, of the general formula:—



where  $R_1$  is an alkyl group and  $R_2$  is an alkyl, carbo-alkoxy-alkyl, aryl, or alkyl, cycloalkyl, cycloalkylalkyl, aralkenyl, or heterocyclic group; or  $R_1$  and  $R_2$  together form a polymethylene or alkyl substituted polymethylene ring; and  $R_3$  is an alkyl or aryl group.

4. 1:3-Divinylhydantoin, of the general formula:—



where  $R_1$  is an alkyl group;  $R_2$  is an alkyl, carbo-alkoxy-alkyl, aryl, aralkyl, cycloalkyl, cycloalkylalkyl, aralkenyl, or heterocyclic group; or  $R_1$  and  $R_2$  together form a polymethylene or alkyl substituted polymethylene ring.

5. 3 - Vinyl - 5:5 - dimethylhydantoin.

6. 3 - Vinyl - 5 - methyl - 5 - ethylhydantoin.

7. 3 - Vinyl - 5 - methyl - 5 - isobutylhydantoin.

8. 3 - Vinyl - 5 - methyl - 5 - phenylhydantoin.

9. 3 - Vinyl - 5 - undecyl - 5 - phenylhydantoin.

10. 3 - Vinyl - 5 - methyl - 5 - cyclohexylhydantoin.

11. 3 - Vinyl - 5.5 - cyclohexylspirohydantoin.

12. 3 - Vinyl - 5.5 - cyclopentylspirohydantoin.

13. 3 - Vinyl - 5:5 - (2 - Methylcyclohexyl) - spirohydantoin.

14. 1 - Vinyl - 3 - ethyl - 5:5 - dimethylhydantoin.

15. 1:3 - Divinyl - 5:5 - dimethylhydantoin.

16. 1:3 - Divinyl - 5 - methyl - 5 - phenylhydantoin.

17. 1:3 - Divinyl - 5 - methyl - 5 - ethylhydantoin.

18. 1:3 - Divinyl - 5 - methyl - 5 - isobutylhydantoin.

19. 1:3 - Divinyl - 5 - methyl - 5 - benzylhydantoin.

20. 1:3 - Divinyl - 5 - methyl - 5 - thienylhydantoin.

21. 1:3 - Divinyl - 5:5 - cyclohexylspirohydantoin.

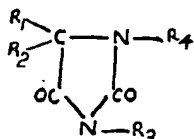
22. 3 - Vinyl - 5 - methyl - 5 - carbethoxy-methylhydantoin.

23. 3 - Vinyl - 5 - methyl - 5 - hexahydro-benzylhydantoin.

5 24. 3 - Vinyl - 5 - methyl - 5 - styryl-hydantoin.

25. 3 - Vinyl - 1 acetyl - 5:5 - dimethyl-hydantoin.

10 26. Process for the preparation of a vinyl-hydantoin of the formula:—



15 where R<sub>1</sub> is an alkyl group and R<sub>2</sub> is an alkyl, carbo-alkoxy-alkyl, aryl, aralkyl, cycloalkyl, cycloalkylalkyl, aralkenyl, or heterocyclic group; or R<sub>1</sub> and R<sub>2</sub> together form a poly-  
20 methylene ring or alkyl substituted polymethylene ring; R<sub>3</sub> is a vinyl group, or an alkyl or aryl group; and R<sub>4</sub> is a vinyl group or an acyl group or hydrogen, at least one of the groups R<sub>3</sub> and R<sub>4</sub> being a vinyl group,  
25 comprising reacting the substituted hydantoin corresponding to the above formula in which the vinyl group or groups are replaced by a hydrogen atom or atoms, in solution or sus-  
30 pension in an inert liquid with acetylene at a pressure within the range 1 to 30 atm. and at a temperature within the range 140—250° C. in the presence of a vinylation catalyst.

27. Process according to claim 26 wherein the catalyst is the cadmium salt of a weak acid.

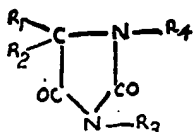
28. Process according to claim 26 wherein the catalyst is the zinc salt of a weak acid.

29. Process according to any of claims 26 to 28 wherein acetylene is continuously pumped through the solution or suspension of the substituted hydantoin held under the required temperature and pressure conditions.

30. Process according to any of claims 26 to 29 wherein both the 1- and 3-positions of the substituted hydantoin are unsubstituted, the amount of acetylene admitted to the reaction being controlled to give a product which consists predominantly of the 3-vinyl derivative.

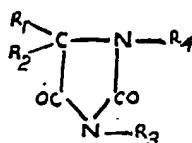
31. Process according to any of claims 26 to 29 wherein both the 1- and 3-positions of the substituted hydantoin are unsubstituted, acetylene being admitted to the reaction until absorption is substantially complete, whereby a product consisting predominantly of the 1:3-divinyl derivative is obtained.

32. Process for the preparation of a vinyl-hydantoin, of the general formula:—



where R<sub>1</sub> is an alkyl group and R<sub>2</sub> is an alkyl, carbo-alkoxy-alkyl, aryl, aralkyl, cycloalkyl, cycloalkylalkyl, aralkenyl, or heterocyclic group; or R<sub>1</sub> and R<sub>2</sub> together form a polymethylene or substituted polymethylene ring; R<sub>3</sub> is a vinyl group, or an alkyl or aryl group; and R<sub>4</sub> is a vinyl group or an acyl group or hydrogen, at least one of the groups R<sub>3</sub> and R<sub>4</sub> being a vinyl group, substantially as hereinbefore described with reference to any of Examples 1, 12, 14, 16, 17, 19, 20, 21, 23, 25, 27, 28, 29, 30, 32, 33, 34, 35, 36, 37, and 39.

33. Process for the preparation of a polymer which comprises polymerising a vinyl hydantoin of the general formula:—

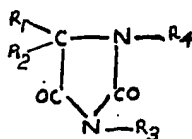


where R<sub>1</sub> is an alkyl group and R<sub>2</sub> is an alkyl, carbo-alkoxy-alkyl, aryl, aralkyl, cycloalkyl, cycloalkylalkyl, aralkenyl or heterocyclic group; or R<sub>1</sub> and R<sub>2</sub> together form a polymethylene ring or substituted polymethylene ring; R<sub>3</sub> is a vinyl group or an alkyl or aryl group; and R<sub>4</sub> is a vinyl group or an acyl group or hydrogen, at least one of the groups R<sub>3</sub> and R<sub>4</sub> being a vinyl group.

34. Process for the preparation of a polymer substantially as hereinbefore described with reference to any of examples 2, 3, 4, 5, 6, 13, 15, 18, 22, 24, 26, 31 and 38.

35. Polymers produced by the process of claim 33 or claim 34.

36. Process for the preparation of a copolymer which comprises copolymerising two or more vinylhydantoins of the general formula:—

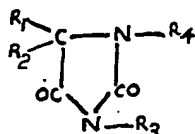


where R<sub>1</sub> is an alkyl group and R<sub>2</sub> is an alkyl, carbo-alkoxy-alkyl, aryl, aralkyl, cycloalkyl, cycloalkylalkyl, aralkenyl, or heterocyclic group; or R<sub>1</sub> and R<sub>2</sub> together form a polymethylene ring or a substituted polymethylene ring; R<sub>3</sub> is a vinyl group or an alkyl or aryl group; and R<sub>4</sub> is a vinyl group, or an acyl group, or hydrogen, at least one of the groups R<sub>3</sub> and R<sub>4</sub> being a vinyl group.

37. Process for the preparation of a copolymer substantially as hereinbefore described with reference to example 40.

38. Copolymers prepared by the process of claim 36 or claim 37.

39. Process for the production of a copolymer which comprises copolymerising at least one vinylhydantoin of the general formula:—



5 where  $R_1$  is an alkyl group and  $R_2$  is an alkyl, carbo-alkoxy-alkyl, aryl, aralkyl, cycloalkyl, cycloalkylalkyl, aralkenyl, or heterocyclic group; or  $R_1$  and  $R_2$  together form a polymethylene ring or a substituted polymethylene ring;  $R_3$  is a vinyl group or an alkyl or aryl group; and  $R_4$  is a vinyl group, or an acyl

group, or hydrogen, at least one of the groups  $R_3$  and  $R_4$  being a vinyl group, with at least one compound containing at least one ethylenic linkage. 10

39. Process for preparing a copolymer substantially as hereinbefore described with reference to any of examples 7, 8, 9, 10 and 11. 15

40. Copolymers prepared by the process of claim 39 or claim 40.

P. L. SPENCER,  
Chartered Patent Agent.

# PROVISIONAL SPECIFICATION

No. 1168 A.D. 1958

## Vinyl Hydantoins

20 We, BRITISH OXYGEN RESEARCH AND DEVELOPMENT LIMITED, a British Company, of Bridgewater House, Cleveland Row, St. James's, London, S.W.1, do hereby declare this invention to be described in the following statement:—

25 This invention relates to chemical compounds and more particularly to vinyl derivatives of the alkyl-substituted cyclic ureides 5:5-dimethylhydantoin and 5-methyl-5-ethylhydantoin and to processes for making them.

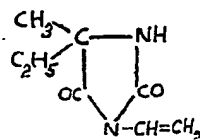
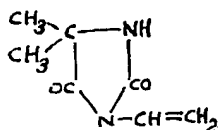
30 Hydantoin was isolated as long ago as 1834 from the leaf buds of *Plantanus Orientalis* and since then hydantoin and many of its derivatives have been synthesised. 5:5-dimethyl- and 5-methyl-5-ethyl-hydantoin can be prepared in good yield from the cheap starting materials acetone and methyl ethyl ketone, respectively, by methods described by E. Ware in Chemical Review, June 1950, Vol. 46, page 413, but this invention is not

restricted to hydantoins prepared by these methods. 40

Hydantoins have many applications, particularly in the medical field. For example, the sodium salt of 5:5-diphenylhydantoin is used as an anticonvulsant. Some hydantoins 45 have a slight hyperglycaemic effect, making them of possible use as a weak antidote to insulin. Hydantoins are also employed in the cosmetic industry and have been suggested for use in textile printing, for polymerisation 50 catalysts, and for the production of resins and plastics by condensation with formaldehyde.

According to one aspect of the invention, there are provided the new chemical compounds, 3-vinyl-5:5-dimethylhydantoin and 3-vinyl-5-methyl-5-ethylhydantoin. 55

According to another aspect of the present invention, a process for preparing 3-vinyl derivatives of 5:5-dimethyl- and 5-methyl-5-ethyl-hydantoin of the following formulae:— 60



65 comprises reacting either 5:5-dimethylhydantoin or 5-methyl-5-ethylhydantoin in solution or suspension in an inert liquid with acetylene in the absence of air at a pressure within the range 1—20 atmospheres and a temperature within the range 140—210° C., and preferably 165—180° C., in the presence of a catalyst. Suitable inert liquids are hydrocarbons such as xylene, benzene or kerosene and suitable catalysts are the cadmium salts of weak acids such as cadmium acetate. A polymerisation inhibitor may be added if desired. Examples of polymerisation inhibitors are hydroquinone, catechol and  $\beta$ -naphthylamine. 75

The vinylation reaction may be effected by saturating the solution or suspension of the substituted hydantoin with acetylene in a

suitable container, such as, for example, a stainless steel autoclave, and maintaining the solution or suspension under the required conditions of temperature and pressure until the required amount of acetylene has been absorbed. 85

During the saturation and subsequent reaction the contents of the vessel should be well agitated, preferably by means of a stirrer or by rocking the autoclave.

Alternatively, the vinylation reaction may be effected by continuously pumping acetylene through the solution or suspension held under the required pressure and temperature conditions in a suitable vessel, the stream of acetylene passing through the liquid serving to agitate the mixture. 90

The 3-vinyl derivative of the substituted

hydantoin is separated from the crude reaction product by distillation and/or recrystallisation from a suitable solvent, which may be the inert liquid used in the reaction. The solvent and residues from the distillation stage may be returned to the reaction vessel and re-used

The method of the present invention is particularly suitable for large scale industrial manufacture. The yields are high and the fact that the unreacted materials may be re-used in a new vinylation cycle improves the overall economy of the process.

Details of the preparation of these new chemical compounds by the method of the present invention are given in the following examples in which all parts and percentages are by weight:—

#### EXAMPLE 1

A stainless steel rocking autoclave (working capacity 1200 cc.) was charged with 5:5-dimethylhydantoin (200 parts), cadmium acetate (10 parts), hydroquinone (2 parts) and xylene (350 parts). After closing the autoclave, the air was flushed out by means of nitrogen and the rocked contents were then saturated with acetylene to 5 atmospheres gauge pressure. The temperature was raised during three hours to 170° C. at which point reaction commenced as indicated by a drop in the pressure. The temperature was maintained at 170—175° C. for 12 hours and the pressure maintained at 18—20 atmospheres gauge by the introduction of further amounts of acetylene. The total fall of pressure over the 12-hour period (i.e. the summation of the several falls from 20 to 18 atm.) was 75 atmospheres. This corresponded to the introduction of about 32 parts of acetylene. (The theoretical amount of acetylene required for the production of 3-vinyl-5:5-dimethylhydantoin corresponds to 33.8 parts).

At the end of the reaction period the autoclave was cooled, the surplus acetylene was vented and the contents of the autoclave were fractionally distilled, firstly at atmospheric pressure to remove xylene and finally at a pressure of 0.7 mm. mercury. 3-vinyl-5:5-dimethylhydantoin (106 parts) distilled as a pale yellow, viscous oil at 110—115° C., followed by a higher boiling fraction (130—

160° C.), which consisted mainly of unchanged starting material (18 parts).

The 3-vinyl-5:5-dimethyl-hydantoin crystallised after standing for a few minutes and it was further purified by recrystallisation from petroleum ether, from which it separated in colourless rhombs, m.p. 94° C.; analysis:—C: 55.0%; H: 6.7%; N: 17.9%; calculated for  $C_7H_{10}N_2O_2$ :—C: 54.6%; H: 6.5%; N: 18.2%. Catalytic hydrogenation in ethanol of 0.3024 gram of the new compound, using palladium on charcoal as catalyst, showed an absorption of 44 ml. hydrogen, which is exactly the calculated amount for a vinyl dimethylhydantoin. The resulting 3-ethyl-5:5-dimethylhydantoin melted at 97° C.; this differs from the melting point of 1-ethyl-5:5-dimethylhydantoin described by Biltz and Slotta in *J. fur Praktische Chem.*, 1926, (2), Vol. 113, page 62, indicating that the vinyl derivative that is prepared is the 3 substituted compound.

#### EXAMPLE 2.

5-methyl-5-ethylhydantoin (110 parts), cadmium acetate (5.5 parts), hydroquinone (2 parts) and xylene (200 parts) were charged to the autoclave of Example 1. After purging with nitrogen the autoclave was pressurised with acetylene to 5 atmospheres gauge. The temperature was raised during three hours to 170° C. and maintained at 170—175° C. for 12 hours, the pressure being maintained at 18—20 atmospheres gauge by the introduction of further acetylene. The total fall of pressure over the 12-hour period was 21 atmospheres. This corresponded to the introduction of about 18 parts of acetylene. (The theoretical amount of acetylene required for the production of 3-vinyl-5-methyl-5-ethyl-hydantoin corresponds to 17 parts). On working up as in Example 1, a 61% yield (80 parts) of the new vinyl compound 3-vinyl-5-methyl-5-ethylhydantoin was obtained as a yellow, viscous liquid, b.p. 106—108° C./0.4 mm., which crystallised in long stout laths, m.p. 33° C. after standing for a week. Found:—N: 16.4%; calculated for  $C_8H_{12}N_2O_2$ :—N: 16.6%.

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Chartered Patent Agent.

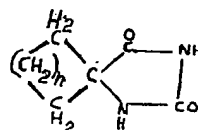
### PROVISIONAL SPECIFICATION

No. 16028 A.D. 1958

### Vinyl Hydantoins

We, BRITISH OXYGEN RESEARCH AND DEVELOPMENT LIMITED, a British Company, of Bridgewater House, Cleveland Row, St. James's, London, S.W.1, do hereby declare this invention to be described in the following statement:—

This invention relates to chemical compounds and more particularly to vinyl derivatives of 5-spirohydantoins of the formula



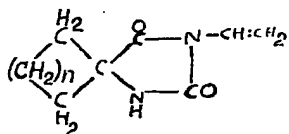
where n is an integer between 2 and 20.

Hydantoins have many applications, particularly in the medical field. For example,

the sodium salt of 5:5-diphenylhydantoin is used as an anticonvulsant. Hydantoins are also employed in the cosmetic industry and have been suggested for use in textile printing, for polymerisation catalysts and for the production of resins and plastics by condensation with formaldehyde.

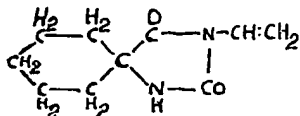
5-Spirohydantoins can be readily prepared from cyclic ketones, potassium cyanide and ammonium carbonate as described in German Patent No. 566,094, but the invention is not restricted to hydantoins prepared by this method.

According to one aspect of the present invention, there are provided the new compounds 3-vinyl-5-spirohydantoins of the formula:—

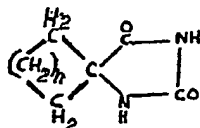


where n is an integer between 2 and 20.

According to another aspect of the invention, there is provided the new compound 3-vinyl-5-cyclohexylspirohydantoin of the formula



According to yet another aspect of the invention, a process for preparing 3-vinyl derivatives of 5-spirohydantoins of the formula



where n is an integer between 2 and 20, comprises reacting the 5-spirohydantoin with acetylene at a pressure within the range 10—30 atmospheres and a temperature within the range 160—220° C. and preferably 180—200° C. in the presence of a catalyst.

Suitable catalysts for the reaction are the cadmium or zinc salts of weak acids such as cadmium acetate and cadmium carbonate. Cadmium oxide may also be used as catalyst. If desired, a polymerisation inhibitor may be added, for example, hydroquinone, catechol, or phenyl β-naphthylamine.

The 5-spirohydantoin may be reacted in solution or suspension in an inert liquid, for example a hydrocarbon such as xylene, benzene or kerosene, or a chlorinated hydrocarbon such as chlorobenzene. The vinylation reaction may be effected by saturating the solution or

suspension with acetylene in a suitable vessel, such as, for example, a stainless steel autoclave, and maintaining the solution or suspension under the required conditions of temperature and pressure until the required amount of acetylene has been absorbed. The contents of the vessel should be well agitated during both the saturation and the vinylation reaction, preferably by means of a stirrer or by rocking the vessel.

The 3-vinyl derivative may be separated from the crude reaction product by distillation at reduced pressure and/or by recrystallisation from a suitable solvent, which may be the inert liquid used in the reaction.

The invention is illustrated by the following example in which all parts are parts by weight.

#### EXAMPLE

Ninety-two parts of cyclohexylspirohydantoin, 5 parts of cadmium acetate, 2 parts of hydroquinone and 260 parts of technical xylene were charged into a stainless steel autoclave. The vessel was then charged with acetylene at 5 atm. The vessel and its contents were rocked and heated during three hours to 160° C., at which point more acetylene was pressed in to bring the pressure to 23 atm. No reaction was evident under these conditions and the temperature was taken to 180° C. at which point a drop in pressure occurred. The temperature was maintained at 180—200° C. and the pressure at 20—23 atm. until a total pressure drop of 29 atms. had taken place in 14 hours.

The cold product from the autoclave consisted of a brown powder (40 parts) and an orange-brown solution. The solid was the required 3-vinyl-5-cyclohexylspirohydantoin ( $C_{16}H_{18}N_2O_2$ ), which was obtained pure by crystallisation from ethanol. It formed colourless needles which melted at 180° C. (Found: C 61.8; H 7.2; N 14.2%, the theoretical values for  $C_{16}H_{18}N_2O_2$  being C 61.8; H 7.3; N 14.4%). The vinyl derivative was further characterised by reducing the vinyl group to an ethyl group by hydrogenation in ethyl acetate in the presence of a palladium catalyst. 0.995 grams of the vinyl compound absorbed 119 ml. hydrogen and yielded the hydride (3-ethyl-5-cyclohexylspirohydantoin), which formed glistening plates (melting at 170° C.) from ethyl acetate. Found: C 61.2; H 8.1; N 14.4%.  $C_{16}H_{18}N_2O_2$  requires C 61.2; H 8.2; N 14.3%).

A further quantity of the vinyl compound was obtained from the brown xylene solution from the autoclave by distillation at 0.4 mm. The fraction boiling at 140—160° C. partially solidified in the receiver and gave 3-vinyl-5-cyclohexylspirohydantoin on triturating with light petroleum.

P. L. SPENCER,  
Chartered Patent Agent.

## PROVISIONAL SPECIFICATION

No. 16029 A.D. 1958

## Vinyl Hydantoins

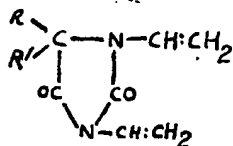
We, BRITISH OXYGEN RESEARCH AND DEVELOPMENT LIMITED, a British Company, of Bridgewater House, Cleveland Row, St. James's, London, S.W.1, do hereby declare this invention to be described in the following statement:—

This invention relates to chemical compounds and more particularly to divinyl derivatives of substituted cyclic ureides, such as 5:5-dimethylhydantoin and 5-methyl-5-phenylhydantoin, and to processes for their manufacture.

Hydantoins have many applications, particularly in the medical field. For example, the sodium salt of 5:5-diphenylhydantoin is used as an anti-convulsant. Hydantoins are also employed in the cosmetic industry and have been suggested for use in textile printing, for polymerisation catalysts and for the production of resins and plastics by condensation with formaldehyde.

5:5-Dimethylhydantoin and 5-methyl-5-phenylhydantoin can be readily prepared in good yield from the readily available starting materials acetone and acetophenone respectively, by methods described by E. Ware in Chemical Reviews, June 1950, Vol. 46, p. 413, but the invention is not restricted to hydantoins prepared by these methods.

According to one aspect of the invention, there are provided the new chemical compounds 1:3-divinyl-5:5-disubstituted hydantoins of the formula:—

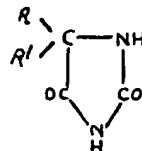


where R and R<sup>1</sup> are alkyl, aryl or aralkyl groups and may be the same or different.

According to another aspect of the invention there are provided the new chemical compounds 1:3-divinyl-5:5-dimethylhydantoin, 1:3-divinyl-5-methyl-5-phenylhydantoin and 1:3-divinyl-5-methyl-5-isobutylhydantoin.

These new compounds, in view of their two vinyl groups which are unsymmetrically placed, are particularly valuable as cross-linking agents in the copolymerisation of two or more polymerisable compounds.

According to yet another aspect of the invention, a process for preparing 1:3-divinyl derivatives of 5:5-disubstituted hydantoins of the formula



where R and R<sup>1</sup> are alkyl, aryl, or aralkyl groups and may be the same or different, comprises reacting the disubstituted hydantoin with acetylene at a pressure within the range of 1—25 atmospheres and a temperature within the range 140—220° C. and preferably 175—190° C. in the presence of a catalyst.

Suitable catalysts include the cadmium and zinc salts of weak acids, such as, for example, cadmium acetate, zinc acetate, and cadmium carbonate. Cadmium oxide may also be used as the catalyst. A polymerisation inhibitor may also be added if desired, examples being hydroquinone, catechol and phenyl-β-naphthylamine.

The disubstituted hydantoin may be reacted in solution or suspension in an inert liquid, for example a hydrocarbon such as xylene, benzene or kerosene or a chlorinated hydrocarbon such as chlorobenzene. The vinylation reaction may be effected by saturating the solution or suspension with acetylene in a suitable vessel, such as, for example, a stainless steel autoclave, and maintaining the mixture under the required conditions of temperature and pressure until no more acetylene is absorbed. The contents of the vessel should be well agitated during both the saturation and the subsequent reaction, preferably by means of a stirrer or by rocking the vessel.

Alternatively, the vinylation reaction may be effected by continuously pumping acetylene through the solution or suspension held under the required conditions of temperature and pressure in a suitable vessel, the stream of acetylene passing through the liquid serving to agitate the mixture.

In certain cases, for example in the case of 5:5-dimethylhydantoin, the vinylation reaction can be carried out in the absence of an inert liquid, the disubstituted hydantoin in the molten state being reacted directly with acetylene. An alternative procedure for separating the 3:5-divinyl derivative is to treat the crude reaction product with cold aqueous alkali, which extracts from the organic solvent phase both unvinylated hydantoin and mono-vinyl derivatives.

The 3:5-divinyl derivative of the disub-

stituted hydantoin may be separated from the crude reaction product by distillation under reduced pressure and/or by recrystallisation from a suitable solvent.

- 5 The N-3 position of the disubstituted hydantoin is vinylated first and by the further action of acetylene the N-1 position is vinylated.

10 The present invention is illustrated by the following examples, in which all parts and percentages are by weight:—

#### EXAMPLE 1

- A stainless steel rocking autoclave was charged with 300 parts of 5:5-dimethylhydantoin, 30 parts of cadmium acetate and 500 parts of xylene. The vessel was tested for leaks by the application of a pressure of 30 atmospheres of nitrogen. The nitrogen was then vented and flushed out with acetylene.
- 20 A pressure of 5 atmospheres of acetylene was applied and heating and rocking of the autoclave was commenced. Absorption of acetylene was apparent at 165° C., at which point further acetylene was pressed in to bring the pressure to 23 atmospheres. The pressure was maintained at 20—23 atmospheres by periodical re-pressurising and the temperature was brought to 175—180° C. and held thereat until the absorption of acetylene has practically ceased. The product consisted of a dark-brown solid suspended in a brownish liquid. The latter was freed from xylene and distilled at a pressure of 1.5 mm. The required divinyl derivative (1:3-divinyl-5:5-dimethylhydantoin) was collected at 98—100° C. It formed a pale yellow oil, which solidified on cooling and gave beautiful long, colourless needles melting at 62—63° C. from light petroleum. Analysis gave C 60.0; H 6.6; N 15.8%, the values required for  $C_8H_{12}O_2N_2$  being C 60.0; H 6.7; N 15.6%.

- The new compound on hydrogenation in ethyl acetate with a platinum catalyst absorbed the calculated volume of hydrogen and yielded 1:3-diethyl-5:5-dimethylhydantoin as colourless, hexagonal plates, melting point 65—66° C. from light petroleum. Analysis of the hydride gave C 58.6; H 8.7; N 15.2%, the values required for  $C_8H_{14}O_2N_2$  being C 58.7; H 8.8; N 15.2%.

#### EXAMPLE 2

- 55 A stainless steel pressure vessel of one litre capacity was charged with 100 parts 5-methyl-5-phenylhydantoin, 5 parts cadmium acetate, 2 parts hydroquinone and 250 parts of technical xylene. Heating and rocking of

the autoclave was commenced at an acetylene pressure of 5 atm. At 165° C. the acetylene pressure was raised to 20 atmospheres and shortly afterwards (at 170—173° C.) absorption of acetylene was apparent by a fall in pressure. The pressure was maintained at 20—23 atmospheres by pressing in more acetylene periodically. The rate of absorption at 170—175° C. fell markedly after eleven hours. The temperature was therefore raised to 200° C. and reaction continued for a further four hours until there was no further pressure drop. The autoclave was allowed to cool to room temperature and the surplus acetylene was vented. The crude product consisted of a mobile, dark brown liquid, which was fractionated at reduced pressure. A yellow, viscous liquid was obtained at 155—159° C./2—3 mm. This substance solidified on cooling and crystallised from ethanol in colourless needles which melted at 88° C. Analysis showed this to be the divinyl derivative of 5-methyl-5-phenylhydantoin (Found: C 69.4; H 5.8; N 11.6%. The divinyl compound  $C_{11}H_{14}N_2O_2$  requires C 69.4 H 5.8; N 11.6%). The compound was further characterised by catalytic hydrogenation: 1 gram of the material absorbed 191 ml. hydrogen and gave a colourless, viscous liquid hydride which was distilled in vacuum for analysis. Found: C 68.3; H 7.4; N 11.4%.  $C_{11}H_{18}N_2O_2$  requires C 68.3; H 7.4; N 11.4%.

#### EXAMPLE 3

In a similar manner to that described in Example 2, 5-methyl-5-isobutylhydantoin (200 parts) was reacted smoothly with acetylene in 10 hours at 183—193° C. and at a pressure in the 18—23 atm. range, using cadmium acetate (10 parts) in xylene (320 parts). The dark brown mobile product was fractionated in vacuo, the main fraction obtained after removal of xylene being 1:3-divinyl-5-methyl-5-isobutylhydantoin (170 parts). This compound is an almost colourless oil which boils at 95° C./0.35 mm. or 65° C./0.05 mm.; it has a refractive index value of 1.5002 at 20° C. and on analysis gave C 65.0%, H 8.2%, N 12.7% ( $C_{15}H_{20}N_2O_2$  requires C 64.8%, H 8.2%, N 12.6%). On hydrogenation in ethyl acetate with a platinum catalyst, the theoretical amount of hydrogen was absorbed. The hydride produced was a colourless oil  $n_D^{20}$  1.4667 (Found: N 12.3%;  $C_{15}H_{22}N_2O_2$  requires N 12.4%).

P. L. SPENCER,

Chartered Patent Agent.

### PROVISIONAL SPECIFICATION

No. 16424 A.D. 1958

### Vinyl Hydantoins

We, BRITISH OXYGEN RESEARCH AND DEVELOPMENT LIMITED, a British Company, of Bridgewater House, Cleveland Row, St. James's, London, S.W.1, do hereby declare

this invention to be described in the following statement:—

This invention relates to chemical compounds and more particularly to vinyl deriva-

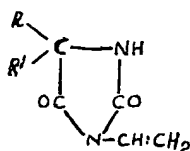


tives of 5-alkyl-5-aryl hydantoin and to processes for the manufacture of such derivatives.

Hydantoin has many applications, particularly in the medical field. For example, the sodium salt of 5:5-diphenylhydantoin is used as an anti-convulsant. Hydantoin is also employed in the cosmetic industry and have been suggested for use in textile printing, for polymerisation catalysts and for the production of resins and plastics by condensation with formaldehyde.

5-Alkyl-5-arylhydantoin may readily be prepared from the appropriate ketone (for example, acetophenone in the case of 5-methyl-5-phenylhydantoin) by methods described by E. Ware in Chemical Reviews, June 1950, Vol. 46, p. 413, but the invention is not restricted to hydantoin prepared by these methods.

According to one aspect of the present invention, there are provided as new chemical compounds 3-vinyl-5-alkyl-5-arylhydantoin of the formula:—



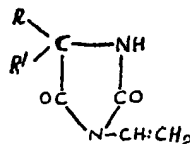
where R is an alkyl group and R<sup>1</sup> is an aryl group.

According to another aspect of the invention, there are provided the new chemical compounds 3-vinyl-5-methyl-5-phenylhydantoin and 3-vinyl-5-undecyl-5-phenylhydantoin.

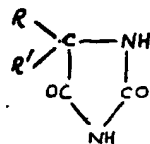
The properties of polymers derived from these new compounds may be modified by substitution in the aryl ring, for example, by sulphonation or nitration.

The presence of a long chain alkyl group in the compound, as, for example, in 3-vinyl-5-undecyl-5-phenylhydantoin, is particularly advantageous for internal plasticisation of polymers or for rendering a polymer hydrophobic.

According to yet another aspect of the invention, a process for preparing 3-vinyl-5-alkyl-5-arylhydantoin of the formula:—



where R is an alkyl group and R<sup>1</sup> is an aryl group, comprises reacting a 5-alkyl-5-arylhydantoin of the formula:—



where R is an alkyl group and R<sup>1</sup> is an aryl group, with acetylene at a pressure within the range of 5 to 30 atmospheres and at a tem-

perature within the range of 140—210° C. and preferably of 165—180° C., in the presence of a catalyst.

Suitable catalysts include the cadmium and zinc salts of weak acids, such as, for example, cadmium acetate, zinc acetate, and cadmium carbonate. Cadmium oxide may also be used as the catalyst. A polymerisation inhibitor may also be added if desired, examples being hydroquinone, catechol and phenyl-β-naphthylamine.

The substituted hydantoin may be reacted in solution or suspension in an inert liquid, for example, a hydrocarbon, such as xylene, benzene, or kerosene or a chlorinated hydrocarbon such as chlorobenzene. The vinylation reaction may be effected by saturating the solution or suspension of the substituted hydantoin with acetylene in a suitable container, such as, for example, a stainless steel autoclave, and maintaining the solution or suspension under the required conditions of temperature and pressure until the required amount of acetylene has been absorbed. The contents of the vessel should be well agitated during both the saturation and the subsequent vinylation reaction, preferably by means of a stirrer or by rocking the vessel.

Alternatively, in certain cases, the vinylation reaction can be carried out in the absence of an inert liquid, the substituted hydantoin in the molten state being reacted directly with acetylene.

The 3-vinyl-5-alkyl-5-arylhydantoin may be separated from the crude reaction product by distillation under reduced pressure and/or by recrystallisation from a suitable solvent.

The invention is illustrated by the following examples in which all parts and percentages are by weight.

#### EXAMPLE 1

Into a stainless steel rocking autoclave was charged 150 parts of 5-methyl-5-phenylhydantoin, 7.5 parts of cadmium acetate, 3 parts hydroquinone and 325 parts of technical xylene. The apparatus was pressure tested by nitrogen, which was then vented and flushed out with acetylene. The vessel was then rocked and heated to 160° C., at which point additional acetylene was pressed in to 23 atmospheres gauge. Absorption of acetylene occurred slowly at this temperature but was hastened by carrying out the reaction at 180—185° C. and 20—23 atm. pressure. The total (summed) pressure drop was restricted to 26 ats. in order to avoid the formation of the 1:3-divinyl derivative.

The product was filtered and the residue (15 parts) was washed with xylene (100 parts). The filtrate and washings were combined and distilled at reduced pressure. The principal fraction boiled at 155—158° C. at 0.3 mm. Hg. and consisted of 125 parts of a pale yellow viscous liquid which was converted into a white solid on trituration with light petro-

leum. The solid was recrystallised from a mixed solvent containing light petroleum and benzene in the ratio 8:1. Colourless crystals, melting point 101—102° C., of 3-vinyl-5-methyl-5-phenylhydantoin were obtained, which gave on analysis C=66.8%, H=5.5%, N=13.0%, the calculated values for  $C_{12}H_{12}N_2O_2$  being C=66.7%, H=5.6%, N=13.0%.

The compound was further characterised by catalytic hydrogenation to 3-ethyl-5-methyl-5-phenylhydantoin, colourless needles, m.p. 104° C. from light petroleum (boiling range 100—120° C.). (Found: C=66.6%, H=6.6%, N=12.9%, the values calculated for  $C_{12}H_{14}N_2O_2$  being C=66.0%, H=6.5%, N=12.8%).

#### EXAMPLE 2

5-Undecyl-5-phenylhydantoin was prepared by heating laurophenone (235 parts) with potassium cyanide (100 parts), ammonium carbonate (200 parts) and 50% aqueous ethanol (400 parts) for 8 hours at 70—80° C. under a carbon dioxide pressure of 40 atm. It formed colourless crystals, m.p. 123° C., from ethanol. Analysis gave C=72.7%, H=9.0%, N=8.3%;  $C_{20}H_{30}N_2O_2$  requires C=72.7%, H=9.15%, N=8.5%.

A mixture of 100 parts 5-undecyl-5-phenylhydantoin, 5 parts cadmium acetate and 350 parts xylene was placed in the autoclave used in Example 1. After pressure testing with nitrogen, the vessel was charged with acetylene to 5 atm. and heated during 3 hours to 165° C. at which point further acetylene was pressed in to bring the pressure to 20 atm. The temperature was raised to the reaction temperature, 185—195° C., and the pressure maintained in the range 20—23 atm. by frequent repressurising until the required amount of acetylene had been absorbed. The crude product from the autoclave was filtered and fractionated at reduced pressure. The vinyl derivative, which boiled at 240° C./0.5 mm., was a viscous liquid of refractive index 1.5242 at 20° C. and mounted to 81 parts. Analysis gave the following result: C=74.4%, H=8.8%, N=7.8%, the theoretical values for  $C_{22}H_{32}N_2O_2$  being C=74.1%, H=9.0%, N=7.9%. Hydrogenation in cyclohexane with a palladium on charcoal catalyst yielded 3-ethyl-5-undecyl-5-phenylhydantoin, refractive index  $n_D^{20}$  = 1.5079.

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#### PROVISIONAL SPECIFICATION

No. 16425 A.D. 1958

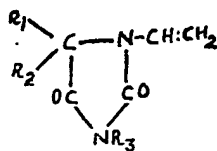
#### Vinyl Hydantoins

We, BRITISH OXYGEN RESEARCH AND DEVELOPMENT LIMITED, a British Company, of Bridgewater House, Cleveland Row, St. James's, London, S.W.1, do hereby declare this invention to be described in the following statement:—

This invention relates to chemical compounds and more particularly to 1-vinyl derivatives of 3:5:5-trisubstituted hydantoins and to processes for the preparation of these derivatives.

Hydantoins have many applications, particularly in the medical field. For example, the sodium salt of 5:5-diphenylhydantoin is used as an anti-convulsant. Hydantoins are also employed in the cosmetic industry and have been suggested for use in textile printing, for polymerisation catalysts and for the production of resins and plastics by condensation with formaldehyde.

According to one aspect of the present invention, there are provided as new chemical products 1-vinyl-3:5:5-trisubstituted hydantoins of the formula:—

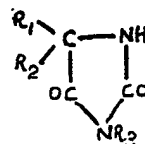


where  $R_1$ ,  $R_2$  and  $R_3$  are alkyl, aryl, or aralkyl groups and may be the same or different.

According to another aspect of the invention, there is provided the new chemical compound 1-vinyl-3-ethyl-5:5-dimethylhydantoin.

These new compounds can be polymerised to new polymeric materials and are therefore of use in the plastics and paint industries. The monomers and the polymers derived from them have substituents on both the nitrogen atoms in the hydantoin ring and are therefore not subjected to enolisation or salt formation. Both monomers and polymers are therefore unaffected by alkalis in the cold.

According to yet another aspect of the invention, a process for preparing 1-vinyl derivatives of 3:5:5-trisubstituted hydantoins of the formula:—



where  $R_1$ ,  $R_2$  and  $R_3$  are alkyl, aryl, or aralkyl groups and may be the same or different, comprises reacting the trisubstituted hydantoin with acetylene at a pressure within the range 5—30 atmospheres, preferably 18—25 atmospheres, and a temperature within the range

170—250°, preferably 200—220° C., in the presence of a catalyst.

5 Suitable catalysts include zinc and cadmium oxides, and zinc and cadmium salts of weak acids, such as the acetates or caprates. A polymerisation inhibitor may also be added, if desired, examples being hydroquinone, catechol and phenyl- $\beta$ -naphthylamine.

10 The trisubstituted hydantoin may be reacted in solution or suspension in an inert liquid, such as xylene, kerosene, or monochlorobenzene. The vinylation reaction may be effected by saturating the solution or suspension of the trisubstituted hydantoin with acetylene in a suitable vessel, for example, a stainless steel autoclave, and maintaining the mixture under the required conditions of temperature and pressure until no more acetylene is absorbed. The contents of the vessel should be well agitated during both the saturation and the subsequent vinylation reaction, preferably by means of a stirrer or by rocking the vessel.

25 Alternatively, the vinylation reaction may be effected by continuously pumping acetylene through the solution or suspension held under the required conditions of temperature and pressure in a suitable vessel, the stream of acetylene passing through the liquid serving to agitate the mixture.

30 In certain cases, the vinylation reaction can be carried out in the absence of an inert liquid, the trisubstituted hydantoin being reacted directly with acetylene.

35 The 1-vinyl derivative may be separated from the crude reaction product either by distillation under reduced pressure, or since it is unaffected by alkali in the cold, by extracting with caustic alkali to remove alkali-soluble material and crystallising the residue from a suitable solvent.

40 The invention is illustrated by the following example in which all parts and percentages are by weight.

#### EXAMPLE

45 A mixture of 3-ethyl-5:5-dimethylhydantoin (prepared by ethylating 5:5-dimethyl-

hydantoin as its potassium derivative with ethyl bromide in a closed vessel in known manner) (100 parts), cadmium acetate (5 parts) and xylene (250 parts) was placed in a stainless steel rocking autoclave. The assembly was then tested for pressure tightness by introducing nitrogen at 30 atm. The nitrogen was afterwards vented off and replaced by acetylene at 5 atm. The vessel was rocked and heat applied. When the temperature reached 180° C. further acetylene was pressed in to bring the pressure up to 20 atm. Reaction was apparent when the temperature had been raised to 200° C. and the temperature was maintained at 200—210° C. until there was no further absorption.

65 The mixture was allowed to cool to about 50° C. and the surplus acetylene was vented. The product was filtered and the xylene removed at 150 mm. pressure. The residue (106 parts) solidified on cooling and it was then dissolved in ether and shaken with 10% caustic soda solution (any unchanged material can be recovered from the alkaline extract). The ether solution was washed with water and dried with anhydrous sodium sulphate. The ether was evaporated off and the residue was crystallised from petroleum ether (boiling range 40—60° C.).

1-vinyl-3-ethyl-5:5-dimethylhydantoin formed colourless laths melting at 65—66° C. Analysis gave C=59.5, H=7.6, N=15.3%, the theoretical values for  $C_{10}H_{14}N_2O_2$  being C=59.3, H=7.7, N=15.4%. The substance absorbed the calculated amount of hydrogen on shaking with hydrogen in ethyl acetate in the presence of a platinum catalyst to yield 1:3-diethyl-5:5-dimethylhydantoin of refractive index 1.4644 at 20° C.

85 In another experiment the crude product of vinylation was fractionally distilled, whereby 1-vinyl-3-ethyl-5:5-dimethylhydantoin was obtained at 90° C./1.5 mm. as a colourless oil which rapidly crystallised on cooling.

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